STRUCTURE, BONDING, AND ADHESION OF MATERIALS INTERFACES WITH DENSITY FUNCTIONAL THEORY: Cr/Fe, SiC/Fe, $MoSi_2$/Ni

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ABSTRACT

SiC/Fe and $MoSi_2$/Ni interfaces are investigated using first principles calculations in order to determine the structure of the interfaces and calculate ideal adhesion energies. As a baseline for comparison, calculations were also performed on the Cr/Fe interface, which shows strong adhesion, even stronger than the intrinsic adhesion of Fe. Both ceramic/metal interfaces show good adhesion. Evidence of Si-Fe and Si-Ni covalent bonding is seen at the respective interfaces.

1. INTRODUCTION

One crucial component to the advancement of military and industrial technologies is the development of new materials and protective material coatings. Strong materials may not be able to withstand certain harsh, corrosive environments as found inside a gun tube or inside a jet turbine engine. Gun tube erosion (GTE) and gas turbine engine coating fracture are two important problems for the military, but developing new protective materials will have a great impact on industry as well.

1.1 GTE and Protective Coatings

The inside of a gun tube is subjected to high temperature (~2500 °C), high pressure, and corrosive blast gases and under these conditions steel erodes quite rapidly (Cote, 2000). Currently, the Army uses a thin protective coating of Cr on the steel due to its high melting point, but the electroplating process used to deposit the Cr on the steel leaves the Cr layer with microcracks. Corrosive blast gases (such as H_2, O_2, CO, CO_2, H_2O, H_2S, and NO_x) penetrate through these microcracks and erode the Cr/Fe interface leading to spallation (flaking off) of the Cr layer. After Cr spalls off the gun tube must undergo maintenance requiring downtime. Cr swept out the gun tube can lead to contamination of the battlefield as Cr will form toxic and carcinogenic chromates in the soil (Blowes, 2002). There is a need for an improved environmental barrier coating (EBC) on steel which protects, not only against high temperature, but also resists chemical attack. A strong, resilient, environmentally safe material that adheres well to Fe is desirable. The coefficient of thermal expansion should be close to, or slightly less than that of Fe.

1.2 Jet Turbines and Thermal Barrier Coatings

Inside a jet turbine the environment is equally harsh with turbine blades exposed to high temperature gases, temperature cycling, and mechanical stresses. Air cooling channels within the turbine blade combined with a thermal barrier coating (TBC) improves the durability and lifetime of turbine blades. The TBC can also allow the engine to operate at temperatures above the melting point of the superalloy, which improves engine performance and efficiency. The current TBC system consists of the substrate (the actual turbine blade, a Ni-based superalloy), a Ni-based bond coat, a thermally grown Al_2O_3 layer, and a Y_2O_3-stabilized ZrO_2 top coat. The thermally grown oxide layer adheres weakly to Ni (Jarvis et al., 2001) and grows during thermal cycling (Brandl et al., 1998). The thickened oxide layer may be responsible for the spallation and failure of the TBC after many such thermal cycles (Pint et al. 1998; Freborg et al. 1998). A new, stronger TBC is desired in order to improve durability of turbine blades, extend their service lifetime, and push the limits of jet engine performance.

1.3 Theoretical Approach to Materials Development

It can be very expensive to build and test new protective materials experimentally, however, predictive calculations can be done rather cheaply. Density functional theory (DFT) is a first principles technique for accurately representing the electronic structure of bulk crystalline solids, including metals. DFT calculations can be used to describe interfacial bonding and predict which material interfaces will be strong. While the calculated ideal adhesion between two materials doesn't account for the plastic deformation that occurs on larger length scales, the trends seen help gauge whether a particular interface is stronger relative to another.

In order to make proper comparisons, we must first examine the current Cr/Fe interface. Identifying the

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reason for the strong adhesion in Cr/Fe can also help focus our search. Previous studies have looked at ceramics as possible protective coatings/liners (Carter, 2006) with ceramic/iron experiments focusing on Al_2O_3/Fe (Dedkov et al., 2002) and MgO/Fe (Faupel et al., 2004). Some previous calculations have investigated metal-carbide and metal-silicide interfaces including ZrC/Fe (Arya and Carter, 2004), TiC/Fe (Mizuno et al., 1998; Arya and Carter, 2003; Lee et al., 2005), and $MoSi_2$/Fe (Jiang and Carter, 2005a). With this in mind we expand our search to include SiC in the present work. Although it has a small coefficient of thermal expansion it is worth considering SiC due to its very high melting point (2970 °C) and high strength.

TBCs involve several layers and several interfaces; numerous experimental and theoretical studies have been performed to characterize the materials and describe the erosion mechanisms (Evans, 2001; Christensen et. al, 2001). Previous work by our group has been aimed at characterizing the interfaces (Christensen and Carter, 2000a; 2000b) and suggesting ways to improve adhesion, e.g., previous DFT calculations have shown that doping the Al_2O_3/Ni interface increases adhesion (Jarvis and Carter, 2002a; 2002b).

The previously calculated strong adhesion of the $MoSi_2$/Fe interface (Jiang and Carter, 2005a), coupled with a very high melting point (2030 °C) makes $MoSi_2$ a possible candidate for TBC on Ni alloys. Other calculations have found good adhesion at the ZrO_2/SiO_2 interface (Jarvis and Carter, 2003) and the $SiO_2/MoSi_2$ interface (Jiang and Carter, 2005b), which means $MoSi_2$ could fit very well into a TBC system consisting of $ZrO_2/SiO_2/MoSi_2$/Ni. We explore the stability of the $MoSi_2$/Ni interface in this work.

2. CALCULATIONAL DETAILS

All calculations were done using the Vienna *ab-initio* simulation package (VASP) (Kresse and Furthmüller, 1996a, 1996b). We performed plane-wave-based, spin-polarized DFT calculations using the all-electron Projector Augmented Wave (PAW) method (Blöchl, 1994; Kresse and Joubert, 1999). The generalized gradient approximation (GGA) is employed for the electron exchange-correlation functional (Perdew et al., 1996).

The total energy is converged with respect to the plane-wave basis set and k-points sampling and all calculations are performed with converged parameters. Calculations of lattice constants and magnetic moments on bulk structures show good agreement with experimental values.

The simulated interface is a periodic supercell which consists of a substrate slab (Fe or Ni), a ceramic coating slab, and a 10 Å vacuum layer. To calculate the ideal work of adhesion, W_{AD}, we calculate the energy difference between the interface and the separated slabs: $W_{ad}=(E_1+E_2-E_{12})/Area$, where E_1 is the energy of the coating, E_2 is the energy of the substrate, and E_{12} is the energy of the coating/substrate system. With this definition, the intrinsic adhesion of a bulk material is simply twice the surface energy, $2\gamma_{surf}$. The lower half of the substrate atoms are kept fixed to bulk parameters while the rest of the atoms are relaxed to within a force tolerance of 0.05 eV/Å. The lattice vectors are kept fixed to bulk substrate parameters for the interface calculations and the separated slabs.

To construct the interfaces, we consider only low energy surfaces since they are more likely to be exposed. We also want to minimize the lattice mismatch since large mismatches will lead to a build-up of strain for thicker layers (Christensen et al., 2001). Taking these two criteria into account, we chose the Cr(001)/Fe(001) and Cr(110)/Fe(110) interfaces for Cr/Fe. We investigated the SiC(001)/Fe(001) interface to model SiC on Fe. We also chose to study the $MoSi_2$(001)/Ni(111), $MoSi_2$(100)/Ni(111), and the $MoSi_2$(110)/Ni(111) interfaces. Generally the number of atomic layers is increased until the value for W_{ad} converges. Another indicator of convergence is when the electronic/structural properties at the center of a slab resemble the bulk properties of that material.

Matching Cr to Fe is simple because both bulk structures are bcc and have very similar lattice constants. In SiC, the C terminated (001) surfaces have a higher surface energy γ, so we used a non-stoichiometric cell to keep a layer of Si atoms at the interface and at the free surface. There are dangling bonds on the (001) surface which may affect the electronic structure at the interface for small slabs. To test this, we created two different SiC/Fe interfaces. One is a clean, bulk-terminated free surface with Si dangling bonds. On the other surface, we formed Si dimers and added H atoms to saturate the dangling bonds. Each dimer formed on the surface has two H atoms, one on each Si. Lone Si adatoms prefer the 4-fold bcc hollow sites on the Fe (001) surface, therefore before relaxation, we shifted the SiC slab to align the Si atoms closer to these hollow sites. There are two distinct (001) cleavage planes in $MoSi_2$ and the surface can be terminated with either all Mo or all Si. The Mo-terminated surface is higher energy, so we constructed the $MoSi_2$ (001) slab of multiple stoichiometric units of Si-Mo-Si layers. On the Ni(111) surface, Si prefers the 3-fold hollow sites over on-top sites. For all three $MoSi_2$/Ni interfaces, the $MoSi_2$ layers were laterally translated to minimize on-top interactions before relaxing the interface.

For all calculations, Fe was set in a fully ferromagnetic (FM) state as a starting guess. The true ground state of Cr is a spin density wave, but we model Cr as the similar bcc anti-ferromagnetic (AF) state which is a more apt description of Cr in the proximity of FM Fe (Walker et al., 1992). SiC and $MoSi_2$ are started with no initial magnetic moments and Ni is started as FM.

3. RESULTS AND DISCUSSION

3.1 Bonding and Adhesion at the Cr/Fe Interface

Calculations on bulk bcc FM Fe and bcc AF Cr predict magnetic moments of 2.2 μ_B and 1.08 μ_B, respectively. Matching the interfaces is straightforward and the mismatch is less than 1%. The Cr slab is under slight compression.

The converged values for W_{ad} were calculated to be 5.37 J/m^2 for Cr(001)/Fe(001) and 5.35 J/m^2 for the Cr(110)/Fe(110) interface. Both values are greater than the intrinsic W_{ad} of Fe of 4.8 J/m^2. The interfaces reached convergence at a thickness of ~20 total atomic layers (10 Cr + 10 Fe). Structural relaxations were mostly small, with the largest relaxations occurring near the interface and at the Cr free surface. The interlayer distance at the interface, Cr_{int}-Fe_{int}, is slightly shorter than in either pure metal, indicating strong heterometallic bonding.

The calculated magnetic moments show a strong spin correlation between Cr and Fe at the interface. At the (100) interface, the first Cr layer exhibits AF coupling to the Fe_{int} layer, with the Cr_{int} atoms having spin opposite to Fe and remaining Cr atoms following the bulk AF arrangement. The magnetic moments of Cr at the center of the slab are very bulk-like with smaller moments near the interface and larger moments near the free surface. The spin on the Fe_{int} atoms is slightly decreased due to proximity to spin-down Cr atoms.

There are both spin-up Cr atoms and spin-down atoms at the Cr(110)/Fe(110) interface. This means the spin-up Cr atoms are slightly frustrated since they are forced to couple ferromagnetically to neighboring Fe atoms. This may be the reason for the slight decrease in ideal W_{ad}. The projected local density of states (DOS) show electron population at the Fermi level, indicating metallic bonding. There is also overlap of bonding and antibonding Cr and Fe d states, which means covalent d-d bonding also contributes to the high interfacial strength (Johnson et al., 2006).

3.2 Bonding and Adhesion at the SiC/Fe Interface

The lattice mismatch of the SiC(001)/Fe(001) interface is only 2.8% with SiC under a small tensile strain. As mentioned, the adhesion energy calculations were performed for two different SiC bulk terminations, bulk-terminated and H-saturated-dimer-terminated. The bulk termination resulted in a calculated ideal W_{ad} of 3.07 J/m^2 and the H-saturated-dimer termination gave a W_{ad} of 2.90 J/m^2.

The Si atoms attempt to relax into the 4-fold hollow sites on the Fe (001) surface, but the rigid structure of SiC prevents a full relaxation. Comparison of the structures of the bulk-terminated and dimer-terminated systems shows only small differences in the atomic positions. No meaningful difference in the electronic structure of the interface occurs either. We believe that the clean terminated surface may give the more reliable value for ideal W_{ad}. The dangling bonds seem to have little impact on the interface, while the strain imposed by the creation of the H-Si-Si-H dimers on the free surface may hinder relaxation of Si atoms at the interface.

Plots of the electron density difference ρ(SiCFe) - ρ(SiC) - ρ(Fe) indicate that upon forming the interface, electron density increases between Si and Fe atoms suggesting that the adhesion strength is partly due to Si-Fe covalent bonding. However, the adhesion is considerably smaller than predicted recently for $MoSi_2$/Fe (3.85 J/m^2, Jiang and Carter, 2005).

3.3 Bonding and Adhesion at the $MoSi_2$/Ni Interface

Three interfaces were studied: $MoSi_2$(001)/Ni(111), $MoSi_2$(100)/Ni(111), and the $MoSi_2$(110)/Ni(111), with lattice mismatches of 3.2%, 2.9%, and 1.3%, respectively. In each case the ceramic is under slight shear strain. Additionally, at the (001) and (100) interfaces, $MoSi_2$ is under slight tensile strain, while $MoSi_2$ (110) is slightly compressed.

The ideal W_{ad} values for $MoSi_2$ (001), $MoSi_2$ (100), and $MoSi_2$ (110) on Ni (111) are predicted to be 3.81 J/m^2, 3.75 J/m^2, and 3.52 J/m^2, respectively. The $MoSi_2$ (110) surface is the lowest energy surface and has the smallest lattice mismatch to Ni (111), suggesting it may be the most likely interface to form. Hence 3.52 J/m^2 may be the most relevant value for the ideal W_{ad}. Electron density difference plots show loss of electron density around the Ni_{int} atoms and an increase in density along the Si-Ni bonds. The projected local DOS shows population at the Fermi level. The strong interfacial adhesion is therefore most likely due to a combination of covalent Si-Ni and Mo-Ni metallic bonding.

CONCLUSIONS

First principles PAW-DFT-GGA calculations were performed for Cr/Fe, SiC/Fe, and $MoSi_2$/Ni interfaces. SiC was found to adhere fairly well to Fe although it is weaker than the Cr/Fe interface. SiC may still be useful as a thin layer in a multilayer EBC system since it is resistant to diffusion of corrosive blast gases. Preventing diffusion of blast gases into the steel microstructure is an important hurdle in developing more durable gun tubes. The $MoSi_2$/Ni interface showed very good adhesion compared to previous calculations of other TBC systems on Ni. A strongly adhered TBC will extend the service lifetime of gas turbine engines and improve performance.

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